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FLUORIDE TECHNOLOGY FOR FABRICATION OF MULLITE ARTICLES FROM QUARTZ-TOPAZ

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The results of studies of fabrication of mullite from quartz-topaz and molding of finished mullite articles directly in the stage of mullitization of topaz concentrate are reported. Using the proposed technology allows manufacturing light-weight refractory articles with a fibrous microstructure and minimizing the number of intermediate operations.

Mullite is increasingly widely used in the technology of high-temperature processes. In particular, mullite refractories are used as lining materials in sintering furnaces [1]. Despite the good thermophysical properties of mullite and the large reserves of the initial mineral raw material, mullite production in our country is in the stage of formation. The needs of the domestic market for mullite are basically satisfied by imports of finished mullite refractories from abroad. There have recently been several studies of the properties of mullite-based ceramics and synthesis of mullite itself [2 – 5].

The results of studies of fabrication of mullite from quartz-topaz by the method of fluoroammonium desilication.

The silicon oxide content in mullite should be 28%[2] according to the empirical formula $3Al_2O_3 \cdot 2SiO_2$, and the initial quartz-topaz concentrate contains 60% silicon oxide. The chemical composition of mullite is (%): 72 Al_2O_3, 28 SiO_2, and the composition of quartz-topaz concentrate is: 30 Al_2O_3, 60 SiO_2, 9 F^-, 1 Fe_2O_3. Since quartz-topaz concentrate is the product of concentration of natural topaz ore, its composition can vary from lot to lot within the limits of 3% as a function of the production site.

The initial quartz-topaz concentrate contains a significant excess of silicon oxide, fluorine, and approximately 1% iron oxide impurity. In calcination of this concentrate at 1400°C, a monolithic ceramic mass is obtained. Mullite in the amount of approximately 60% and cristobalite were found in ground cake by x-ray phase analysis. The mullite crystals have a needle-like structure (Fig. 1). The presence of excess silicon oxide in the quartz-topaz concentrate results in sintering of the material and the necessity of further grinding.

Excess silicon oxide was removed by fluoroammonium desilication. Ammonium bifluoride was added to the initial quartz-topaz concentration, the charge was heated, and the weight losses were determined. Ammonium bifluoride reacts with silicon oxide according to the reaction:

$$SiO_2 + 3NH_4F \cdot HF = (NH_4)_2SiF_6 + 2H_2O + NH_3.$$

The ammonium hexafluorosilicate formed as a result of the reaction passes into the gaseous state above 320°C. Intensive sublimation begins above 500°C. The gaseous ammonium hexafluorosilicate is desublimated and can be regenerated for liberation of ammonium bifluoride. There is a number of studies of desilication methods with ammonium fluorides [6 – 8]. Regeneration of ammonium bifluoride takes place under the effect of ammonia water according to the reaction:

$$(NH_4)_2SiF_6 + 4NH_4OH = SiO_2 + 6NH_4F + 2H_2O.$$

The ammonium fluoride formed as a result of the reaction is evaporated and crystallizes in the form of technical

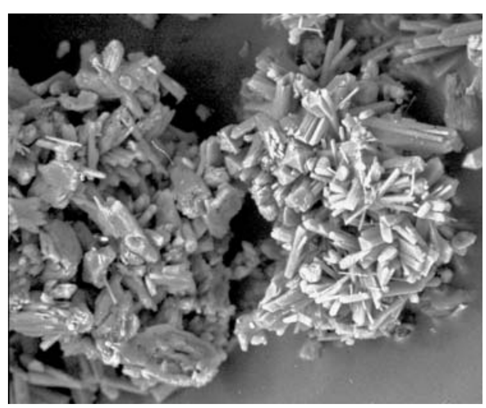

Fig. 1. Photomicrograph of mullite crystals obtained in calcination of quartz-topaz.

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[2] Here and below, mass content.

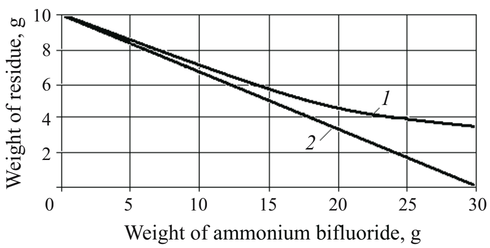

Fig. 2. Change in mass of quartz-topaz concentrate residue as a function of amount of ammonium bifluoride: *1* and *2*) experimental and theoretically calculated results.

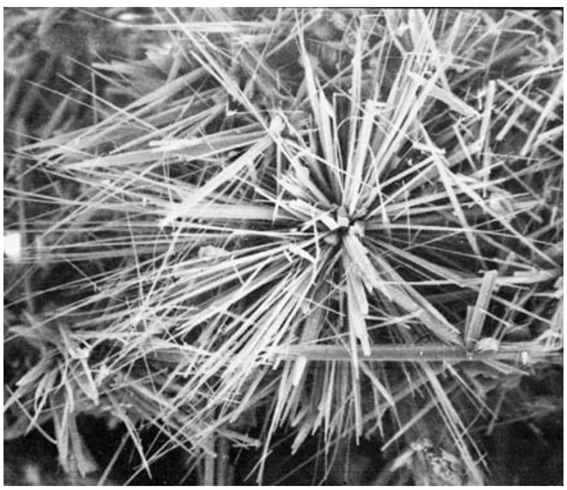

Fig. 3. Photomicrograph of thread-like crystals of mullite obtained after calcination of desilicated quartz-topaz.

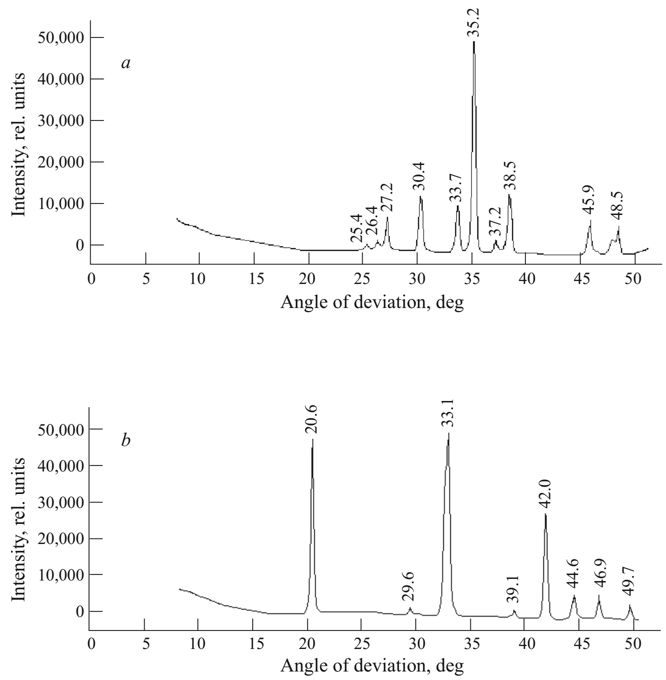

Fig. 4. X-ray pattern of initial quartz-topaz (*a*) and mullite obtained (*b*).

ammonium bifluoride of the composition 25% NH_4F and 75% $3NH_4F \cdot HF$. Silicon oxide is separated in a finely disperse state (so-called silica filler) and can be used in the metallurgical industry as flux or an additive in rubber production.

Studies were conducted to determine the degree of conversion of quartz into ammonium hexafluorosilicate as a function of the amount of ammonium bifluoride in the open system at atmospheric pressure. Samples of quartz-topaz weighing 10 g were blended with a different amount of ammonium bifluoride and placed in numbered porcelain crucibles. The crucibles were placed in a furnace and initially heated to 250°C over 1 h, then the temperature was raised to 900°C for sublimation of the ammonium hexafluorosilicate formed. After standing, the contents of the crucible were weighed. The results obtained are shown in Fig. 2.

We drew the following conclusions from the experimental data:

for insignificant amounts of ammonium bifluoride, complete reaction with quartz and elimination of quartz as ammonium hexafluorosilicate from quartz-topaz take place; this tendency is seen up to the ratio of ammonium bifluoride and quartz-topaz necessary for synthesis of mullite;

when the amount of ammonium bifluoride is exceeded, it begins to react with silicon oxide, entering the structure of the topaz; the rate of this reaction is much lower and the degree of the reaction does not attain 100%, in contrast to the reaction of ammonium bifluoride with the free silicon oxide present in the quartz-topaz concentrate.

Ammonium bifluoride thus converts all of the free silicon oxide into ammonium hexafluorosilicate, which is removed from the system at temperatures above 320°C. An insignificant excess of ammonium bifluoride relative to the stoichiometric amount is necessary for total removal of silicon oxide. Theoretically, 138 g of ammonium bifluoride is required to remove excess silicon oxide from 100 g of quartz-topaz with a 29% aluminum oxide content.

After desilication, the remaining topaz concentrate is a powder with a bulk density of 0.25 – 0.30 kg/dm^3. The significant decrease in the bulk density of the powder after desilication is due to the geological structure of the initial quartz-topaz. Microscopic studies showed that the quartz particles are disseminated in natural quartz-topaz. After the disseminated quartz reacts with the ammonium bifluoride, vacancies and caverns remain in the desilicated mineral, and they are responsible for the important decrease in the density of the powder after desilication. Additional loosening of the structure of the powder charge takes place due to the gaseous products liberated. In calcination of topaz with the excess silicon removed, thread-like mullite crystals are formed (Fig. 3). X-ray phase analysis showed that there is no free silicon oxide in mullite made with this technology (Fig. 4).

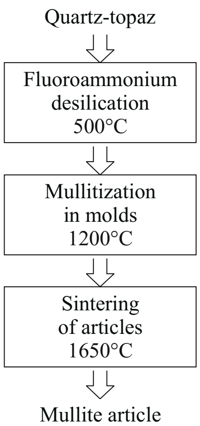

Fig. 5. Sequence of operations in production of mullite from quartz-topaz.

Further studies allowed obtaining mullite articles of the necessary geometric shape. The desilicated intermediate product was poured into a stainless steel mold and heated to 1200°C, where mullitization and partial sintering of topaz took place. The partially sintered product in the form of a block with a compressive strength of 0.5 MPa was removed from the mold and additionally sintered at 1650°C. Mullitization of the block took place at this temperature. The product obtained was a mullite block with a density of 0.4 kg/dm^3. The geometric shape of the block completely matched the shape of the ingot mold. It was thus possible to prepare articles of different shape. The process flow chart for obtaining light-weight mullite articles is shown in Fig. 5.

The bending and compressive strength of the mullite articles was measured.

Force, MPa	**Compression, mm**
5.72	0.57
5.79	0.50
6.38	0.75
6.51	0.87
> 6.51	Fracture

The bending strength of an article was determined on experimental bars with a 10×10 mm section and 40 mm length; it was 5.4 MPa. The maximum sag of the bar before fracture was equal to 0.53 mm.

The advantage of the proposed technology consists of the possibility of obtaining light-weight fibrous mullite articles directly from ore material with a minimum number of operations. Three furnaces with different temperatures or one three-zone furnace are required for setting up a mullite refractory manufacturing section. Regeneration of the ammonium bifluoride allows reducing acquisition costs and the silicon oxide released is an expensive commercial product.

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